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MICROCRYSTALLOSCOPY: QUALITATIVE MICROCHEMICAL
ANALYSIS OF INORGANIC SUBSTANCES

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This 320-page book is authorized by the Ministry of Higher Education USSR as a textbook for chemical specialists in institutions of higher learning. It can also serve as a text for chemists and analysts working in research and plant laboratories, and is useful for persons familiar with qualitative chemical analysis and with the basic concepts of crystallography and crystallochemistry.

INTRODUCTION

Reactions involving 0.01 milligram or less of an unknown substance or ion are considered by chemists to belong in the range of microchemical analysis.

To carry out chemical analysis using micromethods, very small quantities of a determinable substance are required. Therefore, analysis can be carried out in cases where the analyst has only a few grains or drops of the substance available. This circumstance permits one to determine the composition of the substance of finished manufactured articles practically without impairing their external form or weight. The analysis of explosives, fumes, malodorous substances, and the like is associated with some danger or unpleasantness, which is obviated in working with small quantities.

Microchemical analysis can also be of advantage in cases where investigations must be conducted in a short time (which is often necessary). Almost all operations of qualitative microchemical analysis are distinguished by rapid execution, since filtration, vaporization, calcination, and other operations require a very small amount of time.

- 1 -

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Speed and accuracy of the execution of determinations, portability of the apparatus, and negligible expenditure of reagents make microchemical analysis very valuable, and in many cases it is the only possible method of investigation.

Several methods of microchemical analysis are known. Among these are drop analysis, electrocapillary analysis, microcrystalloscopic analysis, and several other methods which have not been used widely. Among micromethods it is necessary to mention also reactions by dry methods, namely, reactions involving the color of flames and reactions in borax beads.

The subject of this book is microcrystalloscopic analysis, a method of qualitative analysis based on reactions in the production of characteristic crystalline precipitates. These precipitates are observed under a microscope, and upon the basis of the external appearance of the crystals a conclusion is reached concerning the presence of unknown or sought-for ions.

The microchemical analysis of steels has been widely employed in practice for about 50 years, ever since the appearance of the classic handbook of the Swedish chemist G. Berens (1895). However, long before G. Berens' work appeared the Russian scientist T. Ye. Lovits (1798) indicated the possibility of conducting qualitative analysis under the microscope, by utilizing the formation of crystalline precipitates. In 1905, Academician D. S. Belyankin published a small monograph, "A Short Handbook on the Microchemical Analysis of Minerals." Microanalysis developed in our country in the 20 years following the appearance of that handbook.

It is possible to introduce a long series of names of Soviet scientists and workers in microchemical analysis who are well known outside the USSR. The works of I. P. Alimarin, S. P. Gvozdev, S. I. D'yachkovskiy, A. S. Komarovskiy, M. O. Korshun, L. M. Kul'berg, L. L. Malyarov, N. A. Tananayev, their co-workers, and others should be noted. The author of this book and his co-workers have written a series of monographs on microchemical analysis and have carried out many experiments.

Part I of this book discusses the problems, important for qualitative analysis, of sensitivity and specificity of reactions and the factors influencing the sensitivity of reactions.

Part II describes well-known microcrystalloscopic reactions for cations and anions. For each ion, the most studied and investigated reactions are noted first, and thereafter the least studied reactions are introduced.

Part III gives examples of the application of the microcrystalloscopic method to qualitative analysis of several important practical objects (alloys, pigments, water).

Part IV contains tables with concise characteristics of the majority of known microcrystalloscopic reactions for cations and anions.

TABLE OF CONTENTS

I. General Part

A. Sensitivity and Specificity of Reactions

Detectable Minimum Quantity
Limiting Concentrations
Other Methods of Expressing the Sensitivity of a Reaction
The Influence of Various Factors Upon the Sensitivity of a Reaction
Limiting Ratios

- 2 -

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B. Methodology and Techniques of Microcrystalloscopic Analysis

Apparatus Used in Microcrystalloscopic Analysis

Reagents

Methods of Microcrystalloscopic Analysis

II. Special Part

A. Cations

Group V: K, Na, NH₄, Li, Mg, Rb, Cs
Group IV: Ca, Sr, Ba
Group III: Al, Cr, Fe, Mn, Zn, Co, Ni, U, Be, Ti, Zr, Th,
Sc, La, Ce, Pr, Nd, Sm, Er, Y, Ta, Nb
Group II: Hg, Pb, Bi, Cu, Cd, As, Sb, Sn, Au, Tl, In, V,
Mo, W, Ge, Te, Se, Pt, Ru, Rh, Pd, Os, Ir, Re
Group I: Ag, Pb, Hg

B. Anions

Group I: HCl, HBr, HI, HCN, Ferrocyanic, Ferricyanic, Rhodanic
Group II: HNO₃, H₂S, HAc
Group III: Sulfurous, Carbonic, Boric, Iodic, Bromic, Oxalic,
Tartaric, Citric, and Pyrophosphoric
Group IV: Phosphoric, Thiosulfuric, Arsenic, Arsenous and
Chromic Acids
Group V: Nitric, Chloric, Perchloric Acids
Group VI: Sulfuric, Hydrofluoric, Fluosilicic Acids
Group VII: Silicic Acids

III. Microchemical Analysis of Some Technical Objects

A. Microchemical Analysis of Water

B. Microchemical Analysis of Metals and their Alloys

C. Microchemical Identification of Inorganic Pigments

IV. Tables of Microcrystalloscopic Reactions

A. Cation Reactions

B. Anion Reactions

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- 3 -

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Results of calculations of relative energies in ionic states are given in Tables 1 and 2 which follow:

Table 1. Energy of the Ionic State of Hydrogen Fluoride

R (A)	0.85	0.95	1.06	1.16	(1.20)	1.27	1.38	1.59	2.16
E_{ion} in kilocalories/mole	77.6	37.5	19.3	13.2	(12.3)	13.9	18.1	31.7	67.1
E_{ion} in electron volts/mole	3.37	1.63	0.84	0.57	(0.53)	0.60	0.79	1.38	2.91

Table 2. Energy of the Ionic State of Hydrogen Chloride

R (A)	1.28	1.59	(1.80)	2.12	2.65
E_{ion} in kilocalories/mole	140.4	75.9	(70.4)	75.2	98.6
E_{ion} in electron volts/mole	6.09	3.29	(3.05)	3.26	4.28

If, from the data in these two tables, the curves $E(R)$ were plotted, the minimum energies and corresponding internuclear intervals would be as follows:

$E_{ion}(H+F-) = 12.3$ kilocalories/mole = 0.53 electron volts/mole; $R_0(H+F-) = 1.2$ A, and

$E_{ion}(H+Cl-) = 70.4$ kilocalories/mole = 3.05 electron volts/mole; $R_0(H+Cl-) = 1.8$ A.

The vibration frequencies of the ionic states were calculated by comparison of curves for the energies of the ionic state and the actual molecule of a hydrogen halide in the range of minimum energy. If experimental values $4,141$ and $2,989$ centimeters⁻¹, respectively, for the frequencies of a molecule of hydrogen fluoride and a molecule of hydrogen chloride are taken, then the vibration frequencies of the ionic states are equal to $2,870$ and $1,500$ centimeters⁻¹, respectively.

On the basis of this data, it was concluded that the ionic states of hydrogen fluoride and hydrogen chloride are characterized by more balanced internuclear intervals and lower amplitudes of vibration frequency than the actual molecules. (The equilibrium internuclear intervals for hydrogen fluoride and hydrogen chloride are 0.92 A and 1.28 A, respectively.)

Obviously, a change in the ionic state (i.e., the polarity, a change in which is equivalent to a change in the coefficient of the wave function describing the ionic state) of the chemical bond must cause a change in both the vibration frequency and the interatomic interval of the chemical bond in such a manner that the magnitude and direction of the change in frequency and internuclear interval depend on the nature of the perturbation.

- 2 -

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In an intermolecular interaction, a change in the polarity depends on the distance between the centers of the molecules and their mutual orientation. In this sense, Batuyev's (4) results are of great interest in showing that the frequency of the hydroxyl group of monomeric fatty acids were the very lowest hydroxyl frequencies in isolated molecules observed up to this time. Later, he tied this up with the tendency of the hydroxyl bond to dissociate and observed that the greater the homopolarity of the hydroxyl bond, the greater its combination frequency; and the greater its electovalency, the lower its combination frequency.

In the case of an increase in the polarity of molecules of hydrogen fluoride, and chloride, a decrease (a displacement to the region of long waves) can be expected in the vibration frequencies of these molecules, not excluding also an increase in the internuclear interval. A displacement of the frequency into the long-wave range during the transition from the gaseous to the liquid state was observed for both halide compounds.

It is concluded that it is necessary to consider the change in the ionic state (polarity) of the chemical bond as one of the reasons for the changes in frequency and also, probably, the internuclear distance which takes place as a result of interactions (intermolecular and intramolecular).

BIBLIOGRAPHY

1. D. B. Hartree, Proc. Roy. Soc., Vol A CLI, p 1935; Vol A CXLI, p 282, 1933
2. E. V. Shpol'skiy, Atomnaya fizika, OGIZ, 202 pp, Moscow-Leningrad, 1944
3. V. M. Dukel'skiy and N. I. Ionov, ZhETF, Vol X, Page 1248, 1940
4. M. I. Vatuyev, DAN, Vol LIX, No 5, 1948
5. L. Pauling, Priroda khimicheskoy svyazi, p 51 ff, Moscow-Leningrad, 1947

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- 3 -

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